

Aliphatic amines suitable as ashless lubricant additives

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Abstract of GB1005638

A lubricant additive comprises an aliphatic amine containing at least two aliphatic or cycloaliphatic polyamine groups, each linked to a hydrocarbon chain of at least 50 carbon atoms by one of its nitrogen atoms. The lubricant may be a mineral lubricating oil, a synthetic lubricating oil or a lubricating oil containing fatty oil. The additive may be added to the lubricant as such or as a concentrate obtained for instance by mixing the product with a small quantity of the oil. Conventional lubricant additives such as anti-oxidants, detergent additives, viscosity-index improvers, anti-corrosives, anti-foaming agents and agents to improve the lubricating effect may be added. In the example an additive obtained by heating a chlorinated ethylene-propylene copolymer with tetraethylene pentamine is added to a solvent-refined paraffinic lubricating oil distillate and then tested in diesel and gasoline engines. Specification 725,169 is referred to. ALSO: An aliphatic amine suitable for use as a lubricant additive contains at least two aliphatic or cycloaliphatic polyamine groups each linked to a hydrocarbon chain of at least 50 carbon atoms by one of its nitrogen atoms. It may be prepared by reacting a halogenated hydrocarbon having at least two halogen atoms as substituents and a hydrocarbon chain of at least 50 carbon atoms with a polyamine, preferably a polyalkylene-polyamine having 3 or more nitrogen atoms. In the example, an ethylene-propylene copolymer is chlorinated and the product is heated with tetraethylene-pentamine. Specification 725,169 is referred to.

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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Aliphatic Amines Suitable as Ashless Lubricant Additives

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the Laws of the Netherlands, of 30, Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to aliphatic amines which are suitable for use as ashless lubricant additives.

Lubricant additives can be divided into compounds containing metal atoms, for instance metal soaps of oil-soluble organic acids, and compounds not containing metal atoms. The latter group of additives contain, instead of metal atoms, a polar organic group, from which they derive their properties as additives. An example of this type of additive is the reaction product of a polymer or copolymer of vinyl chloride and an aliphatic primary or secondary amine with from 6 to 20 carbon atoms, which has been described in British patent specification No. 725,169, which additive, on being added to a lubricating oil, lowers the pour point of that oil and raises its viscosity index.

This invention relates to new compounds that impart to a lubricant detergent properties and also inhibit the formation of sludge in engines running at low load.

An aliphatic amine according to the invention contains at least two aliphatic or cycloaliphatic polyamine groups each linked to a hydrocarbon chain of at least 50 carbon atoms by one of its nitrogen atoms.

By "hydrocarbon chain" is meant a hydrocarbon chain that is at least substantially aliphatic and at least substantially saturated, for instance, alkane chains which may or may not contain aromatic or cycloaliphatic sub-

stituents and, for instance, the chains in polymers and copolymers of olefins.

The distance between any two polyamine groups along the chain is not of essential importance. The distribution of the groups over the chain is usually not regular.

The length of the hydrocarbon chain to which the polyamine groups are linked is important for the solubility of the compound in the lubricant. The fact that solubility is linked up with chain length is easy to establish experimentally. If not more than two polyamine groups are present, a straight non-branched or branched hydrocarbon chain of 100 carbon atoms is usually sufficient for the additive to be soluble in the lubricant to the concentration usually applied for a lubricant additive. With increasing chain length the solubility eventually decreases again. The greatest chain length suitable in this respect depends on the degree of branching and on the degree of crystallinity of the chain. For instance, at the same number of carbon atoms in the chain a compound with a completely atactic polypropylene chain will be more soluble than a compound with an isotactic polyethylene chain. Compounds with a hydrocarbon chain of more than 50,000 carbon atoms may usually be expected to display poor solubility in lubricating oil.

The number of polyamine groups may also have an influence on solubility. Owing to the hydrophilic character of the polyamine group it is understandable that if the number of these groups in the additive molecule increases, while the length of the hydrocarbon remains the same, the oil solubility eventually becomes poor. On this account compounds which have in the chain at least 50 carbon atoms per polyamine group are preferably used.

A highly suitable ratio of the chain length to the number of polyamine groups is one

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polyamine group to, on an average, 200 to 400 carbon atoms in the hydrocarbon chain.

5 The aliphatic polyamine from which the polyamine group has been derived preferably is an amine with two or more nitrogen atoms of which at least one is primary or secondary. Examples of the latter amines are the di-
10 amines 1,2-diaminoethane; 1,2-diaminopropane; 1,3-diaminopropane, the diaminobutanes, the diaminopentanes and their homologues whenever they satisfy the condition that they have at least one primary or secondary nitrogen atom.

15 Of these groups derived from diamines these are preferred which have been derived from N,N-dialkyl-1,3-diaminopropane, for instance, N,N-dimethyl-1,3-diaminopropane.

20 Other examples of amines from which the aliphatic polyamine groups may have been derived are the polyalkylene-polyamines, for example the polyethylenepolyamines, the polypropylenepolyamines and the polybutylenepolyamines. Polyamine groups derived from
25 polyalkylenepolyamine with three or more nitrogen atoms are preferred. Very suitable are the polyamine groups derived from polyethylenepolyamines, in particular those derived from diethylenetriamine, triethylenetetramine and tetraethylenepentamine.

30 Compounds possessing triamine as well as tetramine and pentamine groups can be prepared from technical mixtures of polyethylenepolyamines, which offers economic advantages.

35 The polyamine from which the polyamine groups may be derived may also be a cyclic polyamine, for instance, the cyclic polyamines formed when aliphatic polyamines with nitrogen atoms separated by ethylene groups
40 were heated in the presence of hydrogen chloride.

45 An example of a suitable process for the preparation of the compounds according to the invention is the reaction of a halogenated hydrocarbon having at least two halogen atoms as substituents and a hydrocarbon chain as defined above with a polyamine. The halogen atom is replaced by a polyamine group, while hydrogen halide is formed. The
50 hydrogen halide can then be removed in any suitable way, for instance, as a salt with excess polyamine. The reaction between halogenated hydrocarbon and polyamine is preferably effected at elevated temperature in the presence of a solvent, in particular a solvent having a boiling point of at least 160°C.

55 The reaction between polyhydrogen halide and a polyamine having more than one nitrogen atom available for this reaction is preferably effected in such a way that cross-linking is reduced to a minimum, for instance, by
60 applying an excess of polyamine.

65 Suitable hydrocarbons whose halogen compounds can be used are, for instance, polymers and copolymers of olefins; for instance, halo-

gen compounds of polypropylene, or of copolymers of ethylene and propylene.

The halogenated hydrocarbons can be prepared through halogenation. The starting product is, for instance, a copolymer of
70 ethylene and propylene, 40-60% m of which consists of units originating from propylene; this copolymer is chlorinated to a chlorine content of, for instance, 0.6-1.3% w. The chlorine is linked to primary, secondary and
75 tertiary carbon atoms—substantially to the secondary and tertiary ones—of the hydrocarbon chain.

The lubricant additives according to the invention are excellent dispersants which impart very satisfactory properties to the lubricants in which they are contained. This
80 lubricant may be a mineral lubricating oil of various viscosities, but also a synthetic lubricating oil or a lubricating oil containing fatty oil. The additive may be added to the lubricant as such or as a concentrate, obtained, for instance, by mixing the product with a
85 small quantity of the oil. The concentration of the additive in the oil may vary within wide limits. In general the desired detergent action is brought about if the quantity added is between 0.1 and 10% w, but in special cases larger quantities may be added, for
90 instance, if the lubricating oil is used in diesel engines that are apt to become badly fouled.

When applied as lubricant additives the compounds may be combined with other
95 additives, such as anti-oxidants, detergent additives, viscosity-index improvers, anticorrosives, anti-foaming agents, agents to improve the lubricating effect, and other substances that are generally added to lubricants.

EXAMPLE

Copolymer of ethylene and propylene with tetraethylenepentamine groups as active
100 substituents.

By "active substituents" are meant the
105 organic polar groups from which the compound derives its detergent properties.

The starting material was a copolymer of ethylene and propylene. 50% m (fifty mole per cent) of the copolymer consisted of units
115 originating from propylene, and the copolymer had a mol. wt. of 250,000.

400pbw (parts by weight) of this copolymer were dissolved in 4800 pbw carbon tetrachloride. This solution was, at 50°C, stirred into a solution of 4 pbw chlorine in 500 pbw carbon tetrachloride. After one
120 hour's stirring at 50°C the solvent was removed by evaporation in vacuo at 60°C. Yield: 397 pbw chlorinated copolymer with a chlorine content of 0.90% w.

A solution of 80 pbw of the chlorinated copolymer of ethylene and propylene in 650 pbw o-dichlorobenzene was stirred into 38.3 pbw tetraethylenepentamine at 190°C. While
130

- stirring was continued the temperature was maintained at 190°C for 20 hours. Subsequently, the solvent was removed in a vacuum evaporator at 130°C. The residue was taken up in 260 pbw toluene. The resulting solution was washed with aqueous caustic until the wash liquor was free of chlorine and subsequently with water until neutral. Thereupon the washed solution was poured into 3000 pbw methanol. The precipitate was washed with methanol and dried in vacuo at 60°C. Yield: 82 pbw lubricant additive with a chlorine content of 0.005%w and a nitrogen content of 1.70%w.
- The additive described in the example was tested in a Gardner (Trade Mark) single-cylinder diesel engine and in a Petter (Trade Mark) single-cylinder gasoline engine. The concentration of the additive in the finished lubricating-oil solution was 1.5%w; the base oil was a solvent-refined paraffinic lubricating-oil distillate. The viscosity of the base oil was 7.2 cS at 98.9°C in the Petter test, and 11.5 cS at 98.9°C in the Gardner test.
- Gardner diesel engine.* Water-cooled one-cylinder four-stroke engine, bore 108 mm, stroke 152.4 mm, piston displacement 1.4 litres, power output 11 hp at 1200 revolutions per minute. The duration of the test was 17 hours. The fuel was a gas oil having a sulphur content of 6.9%w. The temperature of the cooling water was 80°C. In this engine the piston fouling was rated.
- Petter gasoline engine.* Water-cooled one-cylinder four-stroke engine, bore 85 mm, stroke 82.5 mm, piston displacement 468 ml, compression ratio 10.0:1, power output 3.5 hp at 1500 rpm. The duration of the test was 48 hours. The fuel was a motor gasoline with 0.32 ml TEL (61.48%w tetraethyl lead, 18.81%w dichloroethane, 17.86%w dibromoethane, balance: colouring matter and kerosine) per litre and a sulphur content of 0.05%w. The temperature of the cylinder cooling water was 80°C, that of the cooling water of the cooled timing gear cover 24°C. In this test the degree of piston fouling and of sludge formation were rated.
- The results of the engine tests are recorded in the table below, which also includes the results obtained with the base oil without additive.

	Petter gasoline engine		
	Gardner diesel piston cleanliness (10=clean)	sludge form (10=clean)	piston cleanliness
base oil + 1.5% additive	8.7	5.9	5.1
base oil	4.4	8.3	7.5

WHAT WE CLAIM IS:—

1. An aliphatic amine suitable for use as an ashless lubricant additive, which contains at least two aliphatic or cycloaliphatic polyamine groups each linked to a hydrocarbon chain of at least 50 carbon atoms by one of its nitrogen atoms.
2. An amine as claimed in Claim 1 in which at least 50 carbon atoms are present in the hydrocarbon chain per aliphatic polyamine group.
3. An amine as claimed in Claim 1 or Claim 2 in which 200 to 400 carbon atoms are present in the hydrocarbon chain per aliphatic polyamine group.
4. An amine as claimed in any of Claims 1 to 3 in which the polyamine groups have been derived from N,N-dialkyl-1,3-diaminopropane.
5. An amine as claimed in Claim 4 in which the polyamine groups have been derived from N,N-dimethyl-1,3-diaminopropane.
6. An amine as claimed in any of Claims 1 to 3 in which the polyamine groups have been derived from polyalkylenepolyamines with at least 3 nitrogen atoms.
7. An amine as claimed in Claim 6 in which the polyamine groups have been derived from polyethylenepolyamine.
8. An amine as claimed in Claim 7 in which the polyamine groups have been derived from diethylenetriamine, triethylenetetramine or tetraethylenepentamine or a mixture thereof.
9. An amine as claimed in any of Claims 1 to 8 in which the hydrocarbon chain is an ethylenepropylene polymer chain of which approximately 50% m consists of propylene units.
10. Aliphatic amines as claimed in Claim 1 and substantially as described.
11. A process for the preparation of an aliphatic amine as claimed in any of Claims 1 to 10 which comprises reacting a polyamine with a halogenated hydrocarbon having at least 50 carbon atoms and at least two halogen atoms as substituents.
12. A process as claimed in Claim 11 in which the halogenated hydrocarbon is pre-

pared by halogenating a copolymer of ethylene and propylene.

13. A process for the preparation of an aliphatic amine substantially as described.

5 14. An aliphatic amine prepared by a process as claimed in any of Claims 11 to 13.

15. A lubricant composition comprising a major proportion of a lubricant and a minor proportion of an aliphatic amine as claimed in any of Claims 1 to 10 or 14. 10

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